Short communication

Effect of nickel impregnated hollow fiber anode for micro tubular solid oxide fuel cells

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HIGHLIGHTS

- A special asymmetrical structure of hollow fiber anode was prepared by the phase inversion technique.
- Surface modification was used to modify hollow fiber anode for micro tubular cells.
- Improved catalytic activity and enhanced electronic conductivity of anode were obtained after Ni impregnation.
- The impregnated micro tubular single cell achieved excellent performance at intermediate temperatures.

ARTICLE INFO

ABSTRACT

A micro tubular solid oxide fuel cells (MT-SOFCs) with a cell configuration of Ni impregnated Ni$-Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC)/GDC/$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)$-$GDC has been prepared by the phase inversion and impregnation technique. A special asymmetrical structure consisting of a sponge-like layer and a finger-like porous layer for hollow fiber anode is obtained by the phase inversion. Fine Ni specie particles are then coated on the surface of anode using impregnation method. The enhancement in electronic conductivity of anode by Ni modification is beneficial to current collection of MT-SOFCs. Meanwhile, the catalytic activity of anode is also improved due to the introduction of Ni nanoparticles. Thus, the Ni modified MT-SOFCs exhibit high power densities, such as 0.69 W cm^{-2} at 600 °C. The encouraging results demonstrate that the Ni impregnation is an effective way to improve anode microstructure of MT-SOFCs.

1. Introduction

In recent years, solid oxide fuel cells (SOFCs) have received tremendous attentions as a keystone of the future energy economy due to their distinct advantages such as extremely high efficiency, low pollution and fuel flexibility [1–6]. Planar and tubular geometric configurations are the most common SOFC designs. The tubular type is relatively mature in terms of designing and manufacturing technology due to its better thermo-cycling and easier sealing behavior, compared to the planar design [7,8]. Interestingly, several potential benefits appear when the diameter becomes smaller, to the micron scale. For example, the micro tubular SOFCs (MT-SOFCs) could achieve higher volumetric power density, better thermal shock resistance, and quicker start-up [9,10]. MT-SOFCs are categorized as anode-supported, electrolyte-supported and cathode-supported structures, depending on the component providing the mechanical strength to the micro-tubular cells. Anode-supported MT-SOFCs are widely favored for the following reasons. They allow for the fabrication of a very thin layer of electrolyte, there is no need to use any sophisticated technique of depositing the electrode inside the micro-tubes and lastly, they facilitate designing current collectors [11]. These characters have promoted the research on anode-supported cells. The development materials of anode-supported MT-SOFCs using nickel (Ni) as the anode catalyst is a very broad for a number of advantages, such as the relatively high electrical conductivity, good catalytic activity and low material cost [12–15].

Note that the microstructure of anode support has great effects on the electrochemical performance of MT-SOFCs. Suzuki et al. [16] reported that the cell's power density enhanced approximately 450% when the size of constituent anode particles was reduced so as to yield a highly porous microstructure and catalytic activity. Li

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et al. [17,18] pointed out that the finger-like voids structure of anode-supported MT-SOFCs which formed during the phase inversion process could significantly enhance the gas diffusion in the anode and lead to high cell performance. Therefore, the ideal microstructure of anode could lead to the high electrochemical performance of MT-SOFCs. Our previous work [19,20] also studied a special asymmetrical structure consisting of a sponge-like layer and a finger-like porous layer as the anode support for MT-SOFCs. However, these anode supports, which were usually co-fired at high temperature with the electrolyte, provide special challenges for avoiding extensive coarsening and sintering. Typical co-fired Ni based cermet anodes had average nickel particle sizes of ~0.5–1 μm, seriously restricting the catalytic activity of anode, especially at low temperature [21]. On the other hand, current collection remained a challenge for MT-SOFCs for practical applications [19,22].

As known, surface modification via solution impregnation process [23–25] is regarded as the most effective and alternative techniques to achieve high activity, beneficial microstructure and good stability in SOFCs electrodes. Herein, we studied the nano-scale nickel (Ni) modified hollow fiber anode for MT-SOFCs. The composite anodes feature nano Ni catalyst coatings supported on the internal surfaces of $Ni-Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) backbones, demonstrating superior catalytic activity for hydrogen oxidation and enhanced electronic conductivity for current collection. Thus, the Ni impregnated anode produced the encouraging results for high performance MT-SOFCs.

2. Experimental

The NiO, $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC), and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) powders were synthesized by auto ignition process [26–29]. Taking the synthesis of LSCF as an example, stoichiometric amount of $La(NO_3)_3$, $Sr(NO_3)_2$, $Co(NO_3)_2$, and $Fe(NO_3)_3$ (Sinopharm Chemical Reagent Co., Ltd) were dissolved in distilled water to form an aqueous solution, citric acid (Sinopharm Chemical Reagent Co., Ltd) and EDTA (Sinopharm Chemical Reagent Co., Ltd) were then added at a molar ratio of citric acid:EDTA:metal of 1:1.5:1, which were used as complexation agent. The mixed solution was heated till self-combustion occurred. The as-synthesized powders were subsequently calcined at 1000 °C for 3 h to obtain fine LSCF powders.

MT-SOFCs with the configuration of NiO–GDC anode, GDC electrolyte, and LSCF–GDC cathode were prepared. NiO and GDC powders were mixed at a weight ratio of 60:40 as the starting materials for the anode substrates. A phase inversion method [30,31] was applied to fabricate the NiO–GDC anode substrates with graded porous microstructure. GDC powders were dispersed into ethanol by ball-milling for 24 h to form a suspension with powders content of 10 wt.%. Subsequently, the suspension was deposited on the outside surface of the anode substrate using a suspension-coating technique [32,33]. After drying, the anode/electrolyte bi-layers were then co-fired at 1400 °C for 5 h to densify the GDC electrolyte. LSCF–GDC (60 wt.% LSCF) powders were mixed thoroughly with 10 wt.% ethylcellulose–terpineol binder to prepare a cathode slurry. The slurry was brush-painted on the GDC electrolyte and fired at 1000 °C for 3 h to form a sandwich tubular structure. Nano-scale Ni species were introduced into the porous NiO–GDC anode backbones by impregnating an aqueous nickel nitrate solution of 0.5 M, followed by calcinations at 800 °C for 1 h. Multiple impregnation of nickel into the backbones were used to introduce a sufficient amount. Nickel oxide was reduced to Ni metal upon exposure to hydrogen fuel. The microstructure features and chemical compositions were obtained with scanning electron microscopy (FEI XL30). Electrical conductivities of anodes were studied using the standard DC four-probe technique on H.P.

multimeter (Model 34401) from 500 to 700 °C. Single cells were tested at 600 °C using humidified hydrogen (~3% H_2O) as the fuel and ambient air as the oxidant. The apparent electrode area was 0.3 cm². An Electrochemical Workstation (Gamry, Interface 1000) was used to characterize the cell electrochemical performance. The electrochemical impedance spectra were measured under open circuit conditions in the frequency range from 1 MHz to 0.1 Hz (10 mV as AC amplitude).

3. Results and discussion

Fig. 1 shows the cross-sectional microstructure of the anode-supported MT-SOFCs. The anode layer presented an asymmetric structure consisting of a finger-like voids layer and a sponge-like layer (Fig. 1a), which was in agreement with the results reported by Li et al. [17] and our previous work [19,20]. The formation of the asymmetric structure could be attributed to the different precipitation rates within the hollow fibers during the spinning process. The rapid instantaneous precipitation occurred on the inner side due to the contact with large quantities of external coagulant, resulting in the formation of the macro voids or the finger-like pores. On the other hand, the slow delayed precipitation on the outer side gave rise to the micro porous structure. Interestingly, this asymmetric structure was propitious to serving as the support for MT-SOFCs. The inside finger-like porous layer could enhance gas diffusion process, and the outside sponge-like porous layer could provide much three phase boundaries (TPBs). The wall thickness of the anode support was about 150 μm. The dense GDC electrolyte layer with the thickness of ~10 μm (Fig. 1b) was obtained using a suspension-coating technique. The cathode was ~26 μm thick. It can be seen that the electrode–electrolyte interfaces display good adhesion to each other. Fig. 1c presents the microstructure of anode without surface modification. The particle sizes in anode supports were coarsening and sintering (>0.5 μm) due to the co-fired process at high temperature (1400 °C for 5 h). In the case of multiple cycles of Ni impregnated anode, fine particles of Ni species with an average particle size of 30 nm were coated on the anode surface (Fig. 1d).

As known, electronic conductivity is an important parameter for the hollow fibers in their role as the anode supports, because the anode fibers not only provide the sites for electrochemical reactions but also serve as current collectors. Fig. 2 shows the electronic conductivities of impregnated Ni-GDC hollow fibers derived at different temperatures measured in H_2 atmosphere. In the case of Ni-GDC hollow fiber, the conductivity decreased with the temperature, which was comparable with other reports [16,19]. As the content of the introduced Ni increased, the conductivity increased. For example, an increase from 480 S cm⁻¹ to 673 S cm⁻¹ (7.4 vol.% Ni impregnated) at 700 °C was obtained. The result indicates that the current collection of the anode support could be significantly improved by Ni surface modification.

Fig. 3 presents the I–V and I–P characteristics of the MT-SOFCs. The open circuit voltage (OCV) values of the micro tubular cells at 600 °C were about 0.75–0.76 V, which were slightly lower than the calculated Nernst voltage (i.e. ~1.1 V at 600 °C). It could be caused by the following two reasons. One is minor electronic conduction through the GDC electrolyte due to the reduction from Ce^{4+} to Ce^{3+} in the reducing atmosphere, which creates short-circuit pathways for the electrons. Another is the possible little diffusion of molecular hydrogen gas through the thin GDC electrolyte with thickness of only 10 μm [34]. However, the OCV values obtained in present study were in very good agreement with the OCVs of the most of the GDC electrolyte based MT-SOFCs that had been previously reported [10,16,17,20,35–37]. The peak power density of the cell before impregnation was 0.28 W cm⁻² at 600 °C. After 7.4 vol.% Ni
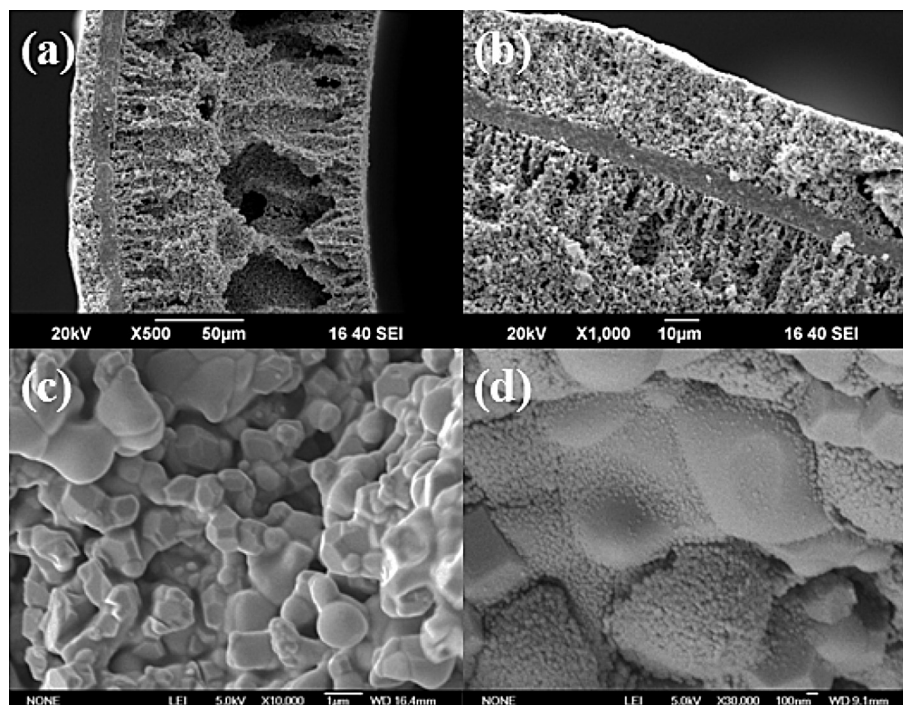
Fig. 1. Cross-sectional views of the anode supported MT-SOFCs, (a) low and (b) high magnification of the fuel cell, the microstructure of anode (c) before and (d) after impregnation.

impregnated, it increased to 0.69 W cm^{-2}. The preliminary result suggests that the surface modification provides an effective and alternative way for improving the anode microstructure for MT-SOFCs.

Fig. 4 presents (a) the impedance spectra as well as (b) the corresponding ohmic resistance, R_o, and polarization resistance, R_p, obtained at 600 °C under open circuit conditions for the tubular cells with different content of Ni impregnation. R_o was reduced after Ni introduced, which was consistent with the study of electronic conductivity in this work. Moreover, R_p was also reduced after Ni impregnated, typically from 0.32 Ω cm^2 to 0.12 Ω cm^2 (7.4 vol.% Ni impregnated) at 600 °C. The LSCF cathode properties of the fuel cells could be assumed constant before and after impregnation. Therefore, the change in R_p was probably due to the variation of polarization resistance of anode. The result is quite reasonable. In the case of Ni impregnated anode, Zhan et al. [38]

studied that increasing the impregnated Ni loading into anode resulted in lower electrode polarization resistance using symmetric anode fuel cells, which could be ascribed to the high TPB density produced by the nano-scale impregnated Ni [39]. However, long-term stability is still a potential issue for the present nano nickel anode, since the easily coarsening of metal Ni particles can potentially reduce the TPBs as well as the electrochemically performance of anode. The development of impregnated microstructure for improving the tolerance towards coarsening and the Ni-GDC co-impregnation technique are the interesting topics definitely deserving further investigation in the future.

4. Conclusions

In summary, surface modification of Ni nano-particles via solution impregnation technique is used to achieve high activity
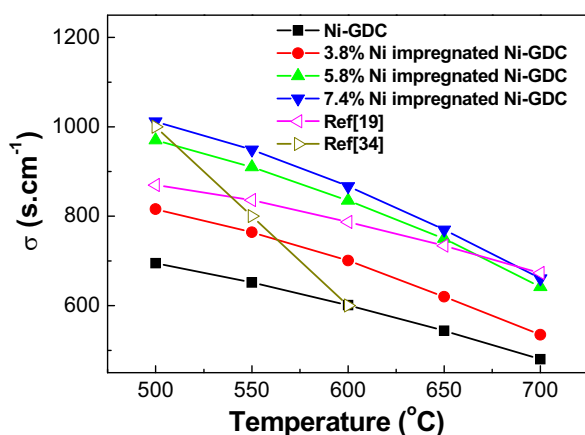

Fig. 2. Temperature dependence of conductivities for hollow fibers with different impregnated Ni loading.
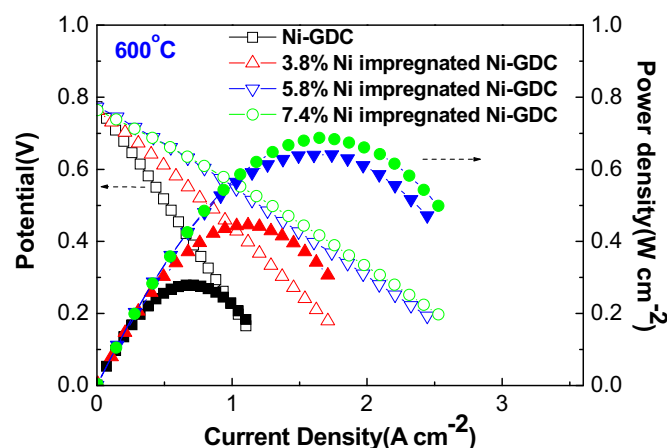

Fig. 3. Typical current–voltage characteristics and the corresponding power densities of MT-SOFCs measured at 600 °C versus the impregnated Ni loading.
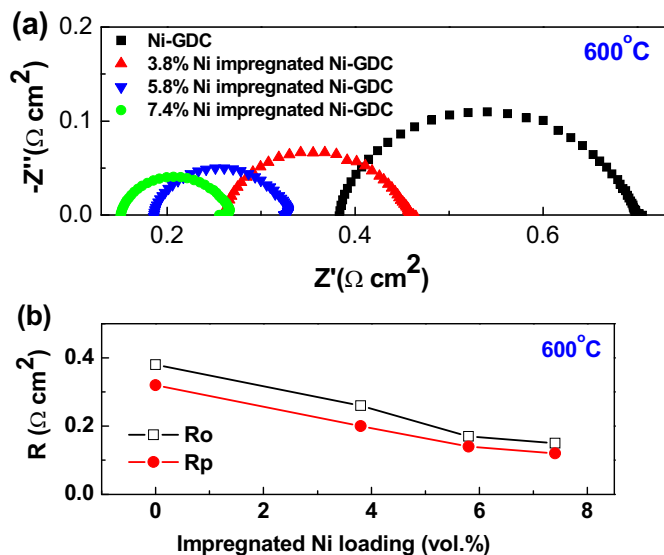
Fig. 4. (a) Impedance spectra of single cells measured under open-circuit condition at 600 °C, (b) ohmic resistance (R_o) and polarization resistance (R_p) obtained from impedance spectra, versus the impregnated Ni loading.

anode for MT-SOFCs. After impregnated, not only electronic conductivity but also catalytic activity of anode are promoted. A micro tubular single cell consisting of a Ni impregnated Ni-GDC anode, a GDC electrolyte, and a LSCF–GDC cathode generates a peak power density of 0.69 W cm^{-2} at 600 °C. The initial results demonstrate that anode microstructure of MT-SOFCs can be effectively modified by the impregnation technique.

Acknowledgment

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